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### Studies on synthesis of aromatic Schiff Bases. Part-IV. Synthesis and characterization of ketimines from 5-chloro-2-hydroxy-4-methyl acetophenone with substituted anilines

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#### ABSTRACT

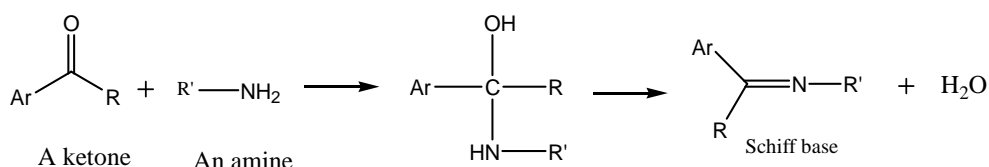
The condensed reaction of aromatic ketone, 5-Chloro-2-hydroxy-4-methyl acetophenone with aniline and its derivatives. Herein the synthesis of ketimines from 5-Chloro-2-hydroxy-4-methyl-acetophenone with Aniline, 3,4-Dimethyl-aniline, 2,4,5-Trichloro-aniline, 4-Methyl-2-nitro-aniline, 4-Methoxy-2-nitro-aniline, 2,3-Dichloro-aniline and 4-Chloro-2-nitro-aniline is reported. These were analyzed by employing the techniques such as colour, physical constant, TLC and spectral techniques(UV-Vis and FTIR).

**Keywords:** Schiff bases, Ketimines, 5-Chloro-4-methyl-2-hydroxy-acetophenone, Aniline, 3,4-Dimethyl-aniline, 2,4,5-Trichloro-aniline, 4-Methyl-2-nitro-aniline, 4-Methoxy-2-nitro-aniline, 2,3-Dichloro-aniline and 4-Chloro-2-nitro-aniline, TLC, UV-Vis and FTIR spectra.

#### INTRODUCTION

A compound formed by the reaction between an aromatic amine and an aldehyde or ketone is known as Schiff base or Ketimines. Schiff bases were first discovered by Hugo Schiff[1] and hence they are referred as Schiff bases. In general the Ketimines are prepared as follows.

Survey of literature indicates that several reviews on the studies of Ketimines or schiff bases have been published[2].The kinetics of formation of Schiff bases in aqueous solution have been extensively studied[3-4]. It has been formed that the reaction is of second order. This reaction proceeds by a two-step mechanism involving a carbinolamine intermediate.



Some schiff bases have been noted to exhibit photochromism and thermochromism and most of these are electrochemistry[5a-5b], fluorescence[6] and luminescence[7], properties of some schiff bases have also been studied. Schiff bases have been investigated by FTIR [8-9] spectra. Many types of reaction like hydrolysis, reduction oxidations, addition, substitution and metal complex formation[10] have been studied with ketimines. Looking to this present study is planned to study of the synthesis of ketimines using 5-Chloro-4-methyl-2-hydroxy-acetophenone with varied substituted anilines.

## MATERIALS AND METHODS

The raw materials ketone, 5-Chloro-2-hydroxy-4-methyl acetophenone and the aniline with Aniline, 3,4-Dimethyl-aniline, 2,4,5-Trichloro-aniline, 4-Methyl-2-nitro-aniline, 4-Methoxy-2-nitro-aniline, 2,3-Dichloro-aniline and 4-Chloro-2-nitro-aniline were of synthesis grades (Sigma-Aldrich) used for synthesis of ketimines. The solvents absolute alcohol, toluene and methanol used for synthesis and in analysis, TLC and UV-Vis spectra purpose were of the synthesis and spectroscopic grade. The reactions were monitored by employing the techniques such as TLC on aluminium plates coated with silica gel 60F<sub>254</sub> (Merck) and UV-Vis monitored on Shimadzu-1800 spectrophotometer. The FTIR spectra were recorded on a Shimadzu FTIR 8400 spectrophotometer (Model-IRAffinity-1) using sample mixed in powder form with KBr powder, the frequency values, 'ν', are in the range of 4000-350 cm<sup>-1</sup>.

The condensation reaction of aromatic ketone, 5-Chloro-2-hydroxy-4-methyl acetophenone with Aniline and its varied derivatives separately each of 0.01 mole in absolute alcohol or toluene on reflux for about 5-6 hrs, gave formation of ketimines. The reaction completion is monitored by employing the techniques such as TLC on aluminium plates coated with silica gel 60F<sub>254</sub> (Merck) visualized by UV cabinet or iodine vapour. The obtained products were purified by column chromatography on 60-120 Silica Gel and employing Toluene and Chloroform as eluent. The physical constants of purified products were determined using digital m. p. apparatus of Equipronics, model, EQ-730 and the colour by visual observation method. The UV-Vis spectra were recorded on Shimadzu-1800 spectrophotometer in alcohol. Stock solutions prepared in absolute ethanol and were of 0.01 M concentration. These solutions were used for the UV-Vis spectral determinations. The structural assignment of the products was based respectively on the elemental (CHN) analysis.

## RESULTS AND DISCUSSION

In the present study, Schiff bases of 5-Chloro-2-hydroxy-4-methyl-acetophenone with Aniline, 3,4-Dimethyl-aniline, 2,4,5-Trichloro-aniline, 4-Methyl-2-nitro-aniline, 4-Methoxy-2-nitro-aniline, 2,3-Dichloro-aniline and 4-Chloro-2-nitro-aniline are synthesized. All the compounds were obtained in high purity. The result of purity indicator of the compounds was ascertained by melting point determinations (open capillary method) and by TLC on Silica gel-G on the glass plate. The structural assignment of the products was based on UV-Vis and FTIR spectral data and elemental (CHN) analyses. The spectral data are in close agreement with the structures of the synthesized compounds. All compounds gave satisfactory elemental analysis i.e. The values are in close agreement with the values calculated for expected molecular formulae assigned to these compounds and are in 5 % in statistics. The analytical results and the % yields for synthesized ketimines are given in **Table-1**.

**Table 1: Analytical Results and % Yields for Synthesized Ketimines, M-I to M-VII derived from 5-Chloro-2-hydroxy-4-methyl-acetophenone**

Sr. No.	Product Code	Aniline	Mol. Wt. of Aniline	Mol Wt of Product,	Wt of Product, gm	% Yield*
1	M-I	Aniline,	93	259.5	8.8	97.56
2	M-II	3,4-Dimethyl Aniline,	121	287.5	5.21	52.10
3	M-III	2,4,5-Trichloro-aniline	196.5	363	3.10	24.54
4	M-IV	4-Methyl-2-nitro-aniline,	149	318.5	11	99.70
5	M-V	4-Methoxy-2-nitro-aniline,	168	334.5	10.74	92.24
6	M-VI	2,3-Dichloro-aniline	162	328.5	1.91	16.71
7	M-VII	4-Chloro-2-nitro-aniline	172.5	339	10.11	85.75

\*isolated yield

The data showing result of synthesis study and their analytical details such as colour and physical constants and TLC for Schiff bases **M-I** to **M-VII**, are depicted in the **Table-2**. Thin layer chromatography indicated single spot TLC for the preparation of the final compounds, **M-I** to **M-VII**, compared with the starting raw material. Thus, the synthesized compounds indicate the homogeneity.

**Table 2: Analytical Results for Synthesized Ketimines, M-I to M-VII, derived from 5-Chloro-2-hydroxy-4-methyl-acetophenone**

Sr. No.	Code No.	Amine used	Colour of Product	Physical constant, °C.	Results of TLC
01	M-I	Aniline	Moss Green	82-90	Single Spot product
02	M-II	3,4-Dimethyl-aniline	Process Yellow	144	Single Spot product
03	M-III	2,4,5-Trichloro-aniline	Brown	68-70	Single Spot product
04	M-IV	4-Methyl-2-nitro-aniline	Orange Red	64-79	Single Spot product
05	M-V	4-Methoxy-2-nitro-aniline	Saddle Brown	58-64	Single Spot product
06	M-VI	2,3-Dichloro-aniline	Light Khaki	66-69	Single Spot product
07	M-VII	4-Chloro-2-nitro-aniline	Dark Orange	74-76	Single Spot product

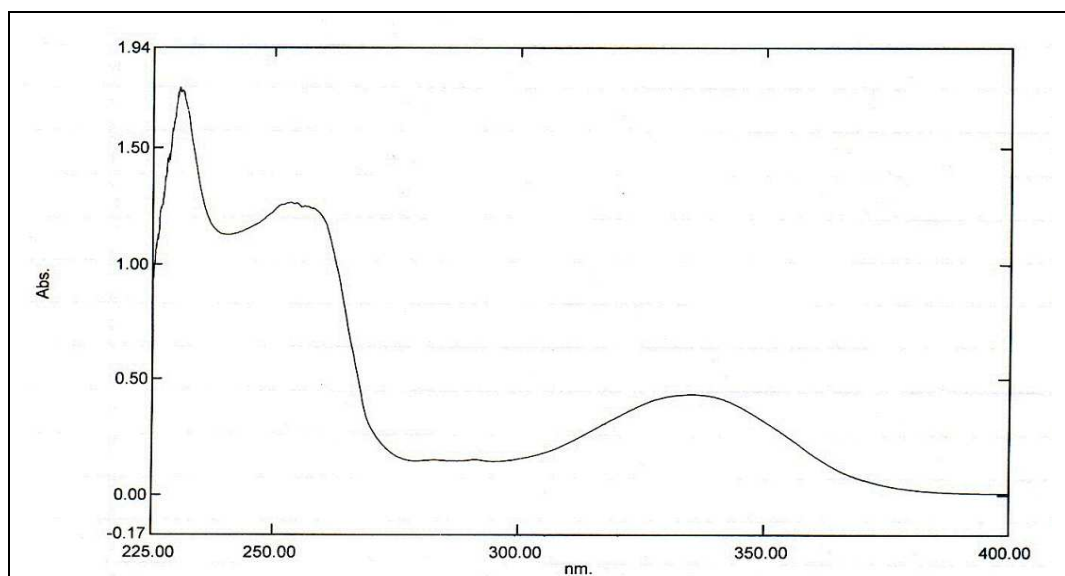
The elemental analysis data for the synthesized ketimines, **M-I** to **M-VII** are indicated in **Table-3**.

**TABLE-3: Data for Elemental Analysis of the Synthesized Ketimines, M-I to M-VII, derived from 5-Chloro-2-hydroxy-4-methyl-acetophenone**

Sr. No.	Code No.	Amine Used	Elemental Analysis of Schiff base					
			% C		% H		% N	
			obs.	cal.	obs.	cal.	obs.	cal.
01	M-I	Aniline	69.25	69.36	5.27	5.39	5.21	5.39
02	M-II	3,4-Dimethyl-aniline	70.21	70.95	6.12	6.30	4.62	4.87
03	M-III	2,4,5-Trichloro-aniline	48.57	49.62	2.76	3.05	3.81	3.86
04	M-IV	4-Methyl-2-nitro-aniline	59.90	60.29	4.50	4.74	8.59	8.79
05	M-V	4-Methoxy-2-nitro-aniline	57.10	57.41	4.55	4.52	8.28	8.37
06	M-VI	2,3-Dichloro-aniline	54.40	54.82	3.56	3.68	4.18	4.26
07	M-VII	4-Chloro-2-nitro-aniline	52.90	53.12	3.51	3.57	8.11	8.26

**Spectral Characterization:** The representative UV-Vis spectra of the synthesized Schiff bases **M-I** is depicted below in **Fig. A**. The related data of UV-Vis characteristic frequency (in nm) indicating the extent of conjugation of the groups in the molecule are indicated in the **Table-4**. Similar observations were made for our earlier report[5b, 9].

**Fig. A: The Representative UV-Vis spectra of the synthesized Schiff bases M-I**



**Fig. B: The Representative FTIR spectra of the synthesized Schiff bases M-I**

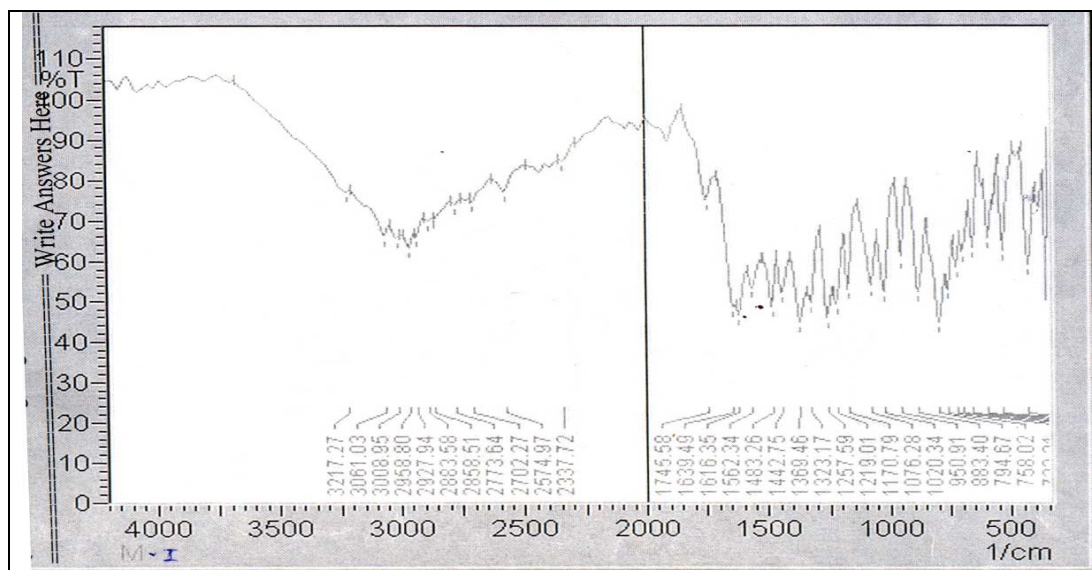


TABLE-4: Analytical Data for Colour and UV-Vis Spectral of the Synthesized Schiff Bases, M-I to M-VII

Sr. No.	Code No.	Colour	UV-Vis ( $\lambda_{max}$ )
01	M-I	Moss Green	335.0, 290.8, 253.1, 230.5
02	M-II	Process Yellow	335.2, 291.2, 232.1
03	M-III	Brown	334.3, 254.5, 231.1
04	M-IV	Orange Red	441.6, 336.4, 251.6, 227.6
05	M-V	Saddle Brown	417.8, 252.0 <sup>ψ</sup> , 279.8,
06	M-VI	Light Khaki	334.9, 257.5, 229.5
07	M-VII	Dark Orange	414.2, 339.8, 232.2 <sup>ψ</sup> , 228.4

<sup>ψ</sup> = shoulder peak

The representative FTIR spectra of the synthesized Schiff bases **M-I** is depicted below in Fig. **B**. The related data of FTIR characteristic frequency (in  $\text{cm}^{-1}$ ) of the groups indicated in the **Table-5**.

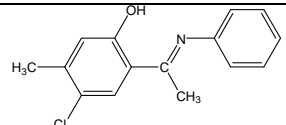
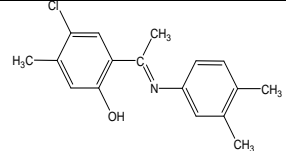
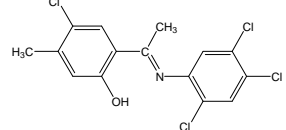
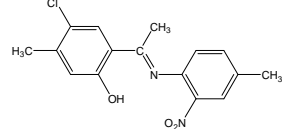
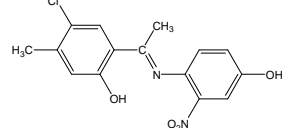
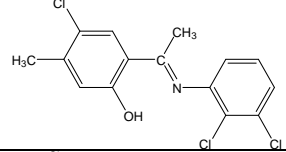
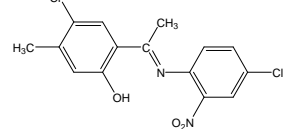
TABLE-5: FTIR Spectral Data of the Synthesized Schiff Bases, M-I to M-VII

Sr. No.	Code No.	IR (in $\text{cm}^{-1}$ )					
		V <sub>&gt;C=N</sub>	V <sub>OH</sub>	V <sub>Ar-CH</sub>	V <sub>C-Cl</sub>	V <sub>NO2</sub>	*
01	M-I	1639	2957-2658	1562-1616, 2958(Ar-C-H stret.)	1076	-	-
02	M-II	1610	2933-2966	1410-1560, 3012 (Ar-C-H stret.)	1085	-	-
03	M-III	1641	2956 3523	1543-1622 2927-2956 (Ar-C-H stret.)	792 1076	-	-
04	M-IV	1641	3459	1571-1597, 2963 (Ar-C-H stret.)	1089	1333	1471
05	M-V	1643	3362	1568-1600, 2921-3051 (Ar-C-H stret.)	1089	1371	1516
06	M-VI	1642	3006-3052	1564-1622, 2966-3111 (Ar-C-H stret.)	1076	-	-
07	M-VII	1624	3386-3479	1502-1562-1600, 2925-2971 (Ar-C-H stret.)	1015-1062	1342	1481

<sup>ψ</sup> = shoulder peak      \* 2<sup>nd</sup> frequency due to -NO<sub>2</sub> group.

From all above characterization one arrives on the following structures of the ketimines synthesized in the present work, as given in **Table 6**. Similar observations were made for our earlier report[5b, 9].

Table 6: Structures of Synthesized Ketimines, M-I to M-VII derived from 5-Chloro-2-hydroxy-4-methyl-acetophenone

I.D. of Comp.	Aniline used, Structure	Name of Schiff Base (Mol. Formula)	Column Elution Solvent, crystal colour
M-I		5-Chloro-2-hydroxy-4-methyl-acetophenoneanil ( $C_{15}H_{14}ONCl$ )	Toluene, Moss Green
M-II		5-Chloro-2-hydroxy-4-methyl acetophenone-3,4-dimethylanil. ( $C_{17}H_{18}ONCl$ )	Toluene, Process Yellow
M-III		5-Chloro-2-hydroxy-4-methylacetophenone-2,4,5-trichloroanil. ( $C_{15}H_{11}ONCl_4$ )	Toluene + Chloroform (85:15), Brown
M-IV		5-Chloro-2-hydroxy-4-methylacetophenone-4-methyl,2-nitroanil. ( $C_{16}H_{15}O_3N_2Cl$ )	Toluene, Orange Red
M-V		5-Chloro-2-hydroxy-4-methylacetophenone-4-methoxy,2-nitroanil. ( $C_{16}H_{15}O_4N_2Cl$ )	Toluene, Saddle Brown
M-VI		5-Chloro-2-hydroxy-4-methyl acetophenone-2,3-dichloroanil. ( $C_{15}H_{12}ONCl_3$ )	Toluene, Light Khaki
M-VII		5-Chloro-2-hydroxy-4-methyl acetophenone-4-chloro,2-nitroanil. ( $C_{15}H_{12}O_3N_2Cl_2$ )	Toluene, Dark Orange

### CONCLUSION

Present work showed condensed reaction of a rare aromatic ketone, 5-Chloro-2-hydroxy-4-methyl acetophenone with aniline and its derivatives such as 3,4-Dimethyl-aniline, 2,4,5-Trichloro-aniline, 4-Methyl-2-nitro-aniline, 4-Methoxy-2-nitro-aniline, 2,3-Dichloro-aniline and 4-Chloro-2-nitro-aniline gave formation of ketimines. The synthesized Schiff base compounds further can be screened for the antifungal activity. These Schiff bases may serve as good intermediates for the Thiazolidin-4-one synthesis and both products may also serves as building block for the further synthesis targets.

### Acknowledgement

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